

WAR DEPARTMENT

TECHNICAL MANUAL



HYDROGEN

TECHNICAL MANUAL }
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HYDROGEN

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SECTION I

GENERAL CHARACTERISTICS

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1. General.—*a.* The efficiency of a gas for balloons and airships is primarily determined by the lift of the gas. This lift depends upon the difference between the weight of the gas in question and the weight of an equal volume of air. Therefore, the lightest gas has greatest lift, and hydrogen, which is the lightest known form of matter, is consequently, in this respect, the ideal gas for use in balloons or airships. It is also essential that any gas used for balloons or airships produce the minimum detrimental effect upon the fabric and materials of which the envelope is made, and that it be readily available at a reasonable price.

b. The element of danger with hydrogen gas is exceedingly great because of its flammable and explosive nature. The best gas, aside from the question of lift, for balloon and airship purposes is helium, a gas nearly as light as hydrogen but possessing none of its dangerous characteristics. At present helium has entirely superseded hydrogen for use in airships operated by this Government. Its production,

*This pamphlet supersedes TR 1170-30, June 29, 1929.

however, is limited and in case of an emergency, when large quantities of lifting gas would be necessary, hydrogen would in all probability be used. Therefore, the latter gas will be considered in detail, as it will probably continue to be used for some time to come in balloon work.

2. Occurrence and sources.—Hydrogen is a very common element in compounds. It forms one-ninth by weight of water and a considerable percentage by weight of oils, of all animal or vegetable compounds, of wood, coal, etc. Since, however, very little free hydrogen is found, it must be separated from other substances with which it is chemically compounded. It is usually produced by decomposition of water.

3. Properties.—*a. Physical.*—(1) Hydrogen is a colorless, odorless, tasteless gas, and therefore cannot be distinguished from air by the senses, except when it contains impurities which may give it a slight color or odor. These impurities are formed in the process of manufacture and may be combinations of sulfur, arsenic, and phosphorus. After use in a rubber envelope, hydrogen frequently has the odor of rubber. Hydrogen is the lightest known form of matter, being 14.4 times lighter than air and 11,124 times lighter than water.

Weight per cubic foot at 32° F. and 29.92 inches barometer (0° C. and 760 mm.) is 0.00559 pound.

Cubic feet per pound at 32° F. and 29.92 inches barometer (0° C. and 760 mm.), 178,931 cubic feet

Specific gravity, 0.06949 (air=1).

Atomic symbol, *H*.

Molecular formula, H_2 .

Freezing and melting point, -434.2° F. (-259° C.).

Boiling point, -421.6° F. (-252° C.).

Coefficient of expansion at constant pressure per degree centigrade (760 mm., 0° to 100° C.), 0.003661 or $1/273.13$.

(2) Because of the lightness of hydrogen it is very mobile and diffuses with great rapidity through other gases. As it has a high rate of diffusion it readily escapes through fine openings. At 77° F. (25° C.) and 30 mm. pressure the diffusion of hydrogen through balloon fabric (rubberized fabric) varies from 8 to 15 liters of hydrogen per square meter per 24 hours.

b. Chemical.—Hydrogen is considered an inert gas because it enters into direct combination with only a few elements, and at ordinary temperatures materials used for containers are not acted on by pure hydrogen. Hydrogen is flammable and will burn in air

when the percentage of it is as low as 4.5 percent; when a mixture of 10 percent or more of oxygen and hydrogen is ignited the flame will be propagated throughout the entire mass and a violent explosion will result. Chlorine gas and hydrogen mixtures when exposed to the sunlight are violently explosive. The violence of all hydrogen-oxygen, hydrogen-air, or hydrogen-chlorine explosions is due to the large amount of energy which is suddenly released when hydrogen combines with oxygen or chlorine. This energy serves to heat the gas to a very high temperature, producing a sudden great change in the volume of the gas which becomes evident in the form of an explosion. When hydrogen combines with oxygen, either the oxygen of the air or in pure form, the product is water. The ignition temperature of mixtures of oxygen and hydrogen varies from 944.6° F. to 1,004° F. (507° C. to 540° C.), electrolytic hydrogen 996.8° F., or 536° C.

4. Flame.—The hydrogen flame is intensely hot, especially when hydrogen is burning in the presence of oxygen rather than with air. The flame of hydrogen burning with oxygen is used for cutting metals, welding alloys, and other operations that can be conducted only at exceedingly high temperatures. It is evident that great care must be exercised when hydrogen is ignited, for the flame may very quickly produce disastrous results if not controlled. The flame of hydrogen burning at moderately low pressure is pale blue or colorless and rather difficult to see, especially in the sunlight, but when the gas is burning at relatively high pressure the flame becomes yellow. In the dark the flame and its characteristics can readily be seen.

5. Lift.—*a. Calculation.*—For ready calculation of the lift of 1 cubic foot of hydrogen the following equation may be used:

$$L = \frac{1.235 \times \text{purity percentage} \times \text{barometric pressure in inches of mercury}}{\text{absolute temperature (F.)}}$$

b. See also TM 1-325 (now published as TR 1170-295) for the lift of gas and the effects of purity, pressure, temperature, and humidity thereon.

6. Laws of gases.—See TM 1-325 (now published as TR 1170-295).

SECTION II

PRODUCTION

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7. General.—*a.* Hydrogen is prepared almost exclusively for practical commercial purposes by the decomposition of water either directly or indirectly. Directly water may be broken up into hydrogen and oxygen by passage of an electric current through water solutions or the hydrogen may be set free from the oxygen by the action of water in the form of steam upon metals at high temperatures. The hydrogen can also be separated from water indirectly in the course of the reaction of certain metals and alloys with strong caustic solutions.

b. In order to be commercially successful, a process for hydrogen generation must produce gas of reasonably high purity containing no constituents, even in small amounts, which are seriously detrimental to the life of the balloon fabrics or material in which the gas is to be used. Since it is much easier to make the gas approximately pure in original manufacture than to separate various impurities from it, the commercial processes for manufacturing hydrogen are limited to those giving substantially pure hydrogen without extensive purification.

c. The process must also require only such materials and equipment as are readily available and can be safely handled without undue danger to operators or difficulty in maintenance of equipment. The speed of production must be adequate, and the process which produces gas most cheaply has a large advantage over other processes.

d. The process in use by the Army for the manufacture of hydrogen for balloon and airship work is the silicon process, in which ferrosilicon (an alloy of iron and silicon) reacts with a strong, hot solution of caustic soda (sodium hydroxide, NaOH).

8. Theory of silicon process.—The production of hydrogen by the use of ferrosilicon, generally known as the "silicon process," de-

depends upon the reaction between silicon, sodium hydroxide (caustic soda), and water with the formation of sodium silicate, called water glass, and hydrogen. Ferrosilicon, which is a mixture of an alloy of silicon and iron, is used instead of pure silicon, because it is possible to produce it more cheaply and easily, and the silicon reacts in the same way as though no iron were present. The ultimate reaction may be regarded as one between silicon and water in which the alkali acts as a catalyzer; that is, a substance which causes the reaction to proceed without itself being used up. The relative amounts of alkali and ferrosilicon to be used in practice cannot be definitely fixed on the basis of a chemical equation, as in the case of most chemical reactions, but are determined by the rate of evolution of the gas desired and the relative cost of the two materials. Ferrosilicon may contain silicon and iron in any proportions and it may be finely or coarsely ground. Consequently, the same weight of material from two different lots will not, in general, yield the same amount of hydrogen. The ferrosilicon used for making hydrogen contains from 70 percent to 90 percent of silicon and the variation in hydrogen yield is even larger, while the rate of reaction of a given weight of material under the conditions of generation may vary by several hundred percent for various materials.

9. Ferrosilicon.—*a. Description.*—Ferrosilicon is an alloy or an intimate mixture of silicon and iron usually containing a number of other elements as impurities. It is made in the electric furnace by heating to a very high temperature a mixture of sand, carbon, and iron or iron oxides. Ferrosilicon is hard and brittle. It has a specific gravity of from 2.5 to 7, depending principally upon composition, the material containing most silicon being the lightest. When used for generating hydrogen, ferrosilicon must be rather finely ground, although it is possible to grind it too finely. A finely powdered material is more likely to cause trouble from foaming and by clogging the generator than is a coarse material, but it has the advantage of permitting the generator to be brought to a favorable operating temperature more quickly. There is also some economy of material in the use of the pulverized ferrosilicon.

b. Test.—Ferrosilicon is purchased on specifications, and will, in general, be tested by the purchasing department and supplied to the air stations, accompanied by all necessary directions for use. There will, therefore, rarely be occasion for tests of the material by those for whose use these regulations are primarily intended.

c. Packing, shipping, and storing.—(1) Ferrosilicon cans should contain not more than 150 pounds each.

(2) If ferrosilicon were always pure, no danger whatever would attend the shipment and storage, but it always contains small amounts of other compounds, notably calcium carbide and calcium phosphide, which produce dangerous gases in moist air. Consequently, ferrosilicon should be shipped and stored in dry, well-ventilated compartments.

(3) Ferrosilicon and sodium hydroxide should never be stored together where there is any possibility of their becoming mixed by the breaking of one or more packages, as the resulting mixture would create a fire hazard.

10. Sodium hydroxide or caustic soda.—*a.* Caustic soda is a material familiar to the majority of people. It is a white solid which absorbs water from moist air and will ultimately dissolve if exposed to the air very long. A considerable amount of heat is produced when sodium hydroxide dissolves, and this heat of solution is relied upon to start the reaction with ferrosilicon. In the presence of insufficient water to completely dissolve it, sodium hydroxide will form a solid cake which is very difficult to handle in any way. When exposed to air, sodium hydroxide takes up carbon dioxide as well as water and forms sodium carbonate. While this compound will react with ferrosilicon to produce hydrogen, it does not react vigorously; it may produce carbon dioxide when used in dilute solution; and it is precipitated in a strong solution of hydroxide. The carbonate present in a sample of sodium hydroxide is therefore nearly useless for the generation of hydrogen. Caustic soda is supplied in airtight containers and should not be exposed to the atmosphere. Containers should be opened only as the material is required. Sodium hydroxide is very corrosive either in solid form or in solution. It irritates the skin and may cause blindness if it gets in the eyes. It will destroy clothing, especially wool and leather. Its injurious effects may be quickly counteracted by the use of an acid such as vinegar, but care must be taken that the acid used is not in so concentrated a form to produce as serious results as those of the alkali.

b. Sodium hydroxide should be packed in airtight iron cans or drums preferably containing not more than 100 pounds each. Each drum should be tightly soldered. A drum once broken open should be used immediately or the contents transferred to an airtight container. The material should always be stored in a dry place under cover. Ventilation is not as important as in the case of ferrosilicon. (See par. 9c (3).)

11. Conditions affecting rate of reaction per unit weight of ferrosilicon.—*a.* The rate at which hydrogen is produced from a

given weight of ferrosilicon in the generator is of the greatest importance in determining the best method of generator operation. The influence of various conditions upon this rate of reaction per unit weight of ferrosilicon is described in the following paragraphs.

b. The rate of reaction increases with increasing silicon content in the ferrosilicon up to about 90 percent silicon. Material containing more than this amount of silicon reacts less rapidly. The rate of reaction of material containing less than 75 percent of silicon is very slow.

c. The rate of reaction is greater for finely powdered than for a coarse material.

d. The rate of reaction of material introduced into a fresh sodium hydroxide solution increases with increasing concentration of sodium hydroxide, but there is little advantage in this respect in using a solution stronger than 35 parts of sodium hydroxide to 100 parts of water and almost none in using more than 40 parts of alkali to 100 parts of water. As the reaction proceeds and sodium silicate is formed more water must be added, otherwise the "water glass" makes the solution so viscous that the reaction is slowed down, there is trouble from foaming, and the sludge may even solidify inside the generator. Even under the most favorable conditions the rate of reaction falls off as the sodium hydroxide is used up unless an excessive amount of sodium hydroxide is used.

e. The rate of reaction increases very rapidly with increasing temperature. At 100° C. it is about twelve times as rapid as at 60° C., and there is an increase of 50 percent from 100° C. to 110° C.

f. With a given sample of ferrosilicon the rate of reaction is always directly proportional to the amount of material in the generator which is being acted upon.

12. Temperature changes.—The reaction by which hydrogen is produced is accompanied by the production of a large amount of heat. Consequently, if the temperature of the generator is low when the reaction starts it will gradually increase without the application of external heat. Since the rate of reaction increases rapidly with increasing temperature, both the rate of reaction and the temperature are rapidly accelerated and the reaction becomes violent in the presence of a sufficient amount of reacting material. The temperature increase is strictly limited, however, by the heat losses from the generator, by far the most important of which is due to the evaporation of water. When gas escapes from water or any volatile liquid, it carries with it some of the liquid in the form of a vapor. The volume of vapor carried away in this manner has the same ratio to the

total volume of gas and vapor that the vapor pressure of the liquid has to the barometric pressure. The boiling point of a liquid is temperature at which the vapor pressure becomes equal to the atmospheric pressure. Therefore, the temperature of the liquid from which the gas is escaping can never quite reach the boiling point, since at the boiling point the escaping gas must consist entirely of vapor. A large amount of heat is required to convert water into vapor. It is apparent that the temperature of the generator can never reach the boiling point of the solution, and that if the reaction is once fairly started and the other generator conditions are kept constant the temperature must quickly reach an equilibrium value at which the heat losses exactly balance the heat of reaction.

13. Amount of reacting material.—*a.* The total rate of generation under any given conditions is proportional to the amount of ferrosilicon in the generator. If the generator conditions are kept constant while adding ferrosilicon at a constant rate, the rate at which the ferrosilicon is acted upon must become equal to the rate of addition. If the rate of addition is in excess of the rate of consumption, ferrosilicon will accumulate until the two rates become equal; if the rate of consumption is in excess of the rate of addition, the amount of ferrosilicon in the generator will decrease until equilibrium is again established.

b. The result desired in the operation of a generator is to produce gas at a uniform rate from the beginning of the run to the end without wasting time or materials, and the operating conditions must be chosen to approximate this ideal condition as closely as possible.

14. Most favorable conditions for operation.—*a.* The heat of solution of sodium hydroxide is not sufficient to raise the temperature of the generator to a point favorable for the reaction. The reaction is therefore necessarily slow at the start. The only material wasted is that remaining unacted upon at the end of the run when the reaction becomes too slow to justify further loss of time in waiting for its completion. Hence, three requirements are to be met in generator operation.

(1) The temperature is to be brought up to the working value as quickly as possible.

(2) An equilibrium between the rate of addition and consumption of ferrosilicon is to be established and maintained until the end of the run.

(3) The equilibrium conditions are to be so chosen that the amount of ferrosilicon and sodium hydroxide remaining in the generator at the end of the run shall be a minimum.

b. The conditions necessary to fulfill these three requirements will now be considered in the reverse order.

(1) Economy as to the amount of sodium hydroxide used requires that the concentration of the solution be kept low (not more than 25 to 30 parts of sodium hydroxide to 100 parts of water) during the latter part of the run.

(2) With a solution of given strength at the end of the run, economy of ferrosilicon requires that the temperature be as high as possible at the end of the run. This maximum temperature can be obtained only by allowing the thermal equilibrium to become established automatically.

(3) A uniform rate of gas evolution, which is desirable from several standpoints, can be obtained in practice only by keeping the rate of ferrosilicon feed and the temperature nearly constant during the run.

(4) The previous requirements make it necessary to maintain the temperature of the generator during the major part of the run a little below the temperature at the end of the run.

(5) In order to avoid a waste of time at the beginning of the run the temperature of the generator must be quickly raised to the operating temperature. Much water is evaporated during the run. If no water were added during the run, the condition in (1) above would require a very dilute solution at the start. It is impossible, however, to get the temperature of a dilute solution quickly up to the operating temperature. It is, therefore, necessary to start with a concentrated solution and to dilute with water during the run; the rate of ferrosilicon feed being correct, the proper operating temperature may be maintained throughout the run by this method. See paragraph 19*d*.

(6) The temperature at the start can be most quickly raised to the operating temperature by introducing a comparatively large amount of ferrosilicon. In order to get a uniform rate of evolution it is necessary that this initial charge of ferrosilicon is so chosen that the following condition will be approximated as closely as possible, viz, when the temperature of the generator reaches the operating temperature, the amount of ferrosilicon present shall be just sufficient to react at the predetermined rate at which ferrosilicon is to be fed into the generator.

15. How to determine when method of operation should be changed.—*a.* A set of instructions is given specifying—

(1) Initial concentration of solution.

(2) Initial charge.

- (3) Rate of feed.
- (4) Operating temperature.
- (5) Manner of water cooling.

Some or all of these factors may have to be varied under certain conditions as experience dictates. If the operator has some means of determining temperature and rate of gas evolution, it is easy to determine when any of these conditions are at fault, as shown in the following paragraphs.

b. If an excessive amount of time is required to get the sodium hydroxide into solution, and particularly if the temperature in the mixing tank passes through a maximum before solution is complete, the solution is being made too concentrated. If the alkali goes into solution promptly, and there is difficulty in starting generation when the solution is run into the generator, the solution may advantageously be made more concentrated.

c. When the temperature of the generator reaches the operating temperature, the ferrosilicon feed is started. If the rate of gas evolution decreases during the next few minutes, while the temperature is kept constant, the initial charge was too large. If the rate increases, the initial charge should be increased. (See pars. 14*a* and 19*d*.)

d. If the gas leaving the washer is at a temperature much above that of the wash water, or if there is any noticeable amount of alkali spray in it, the rate of ferrosilicon feed is too high. If the gas comes out at the temperature of the wash water and is free from impurities, and the rate of gas evolution is considerably less than that for which the washer was designed, the rate of ferrosilicon feed is too low.

e. If much cooling water is required to maintain the operating temperature until the end of the run, and the temperature rises rapidly if the cooling water is shut off for a short time near the end of the run, the operating temperature is too low. If cooling water is required only during the first part of the run, and the sludge is very viscous or solidifies on cooling, the operating temperature is too high.

f. If, when the cooling water is shut off, the temperature rises quickly several degrees, and a viscous sludge is found at the end of the run, more cooling water should be used. If, after the cooling water is shut off, the temperature falls and the reaction slows down very considerably before all the ferrosilicon is added, less cooling water should be used.

16. Computing quantities for charge.—*a.* The officer or non-commissioned officer in charge should understand fully the effect of

variations in quality of ferrosilicon and be able to calculate the proportion of caustic soda required. He should also understand the effect of various factors, as discussed, so as to be in position to make economies in materials during periods when speed is not essential. He should keep posted on experimental work that is being carried on, and change his methods accordingly.

b. According to some tests carried out at the Bureau of Standards the weight of ferrosilicon to produce 1,000 cubic feet of hydrogen measured at different temperatures is as follows:

Pounds of ferrosilicon per 1,000 cubic feet

Temperature of gas	Silicon in ferrosilicon			
	75 percent	80 percent	85 percent	90 percent
32° F.....	78. 2	65. 5	52. 0	44. 4
60° F.....	73. 0	58. 5	48. 5	41. 5
70° F.....	71. 0	57. 0	47. 0	40. 5
80° F.....	69. 0	55. 0	46. 0	39. 5
90° F.....	67. 0	53. 5	44. 0	38. 0

These values will vary somewhat in field work, and under ordinary conditions where a gas holder or nurse balloon is available there is no necessity for changing the size of the charge. Theoretically it would require 2.8 pounds of caustic soda for 1 pound of ferrosilicon, but for reasons explained previously a much smaller quantity has been found to give complete reaction. Experiments have determined that 1.4 pounds of caustic soda to each pound of ferrosilicon will produce nearly as much gas as the theoretical quantity of caustic soda in the same time, and under the best conditions the quantity may be cut down to 0.9 pound per pound of ferrosilicon. A proportion of from 1.3 to 1.5 parts of sodium hydroxide for each part of 80 percent ferrosilicon may be considered as good operating practice.

c. The following steps should be taken to prepare for a run :

(1) Compute the total generator charge to be used for a single run from the volume of gas desired and the total yield obtainable from the material.

(2) Compute the rate of ferrosilicon feed from the total yield per unit weight of material and the capacity of the washer cooler system, on the assumption that the rate of consumption of material will equal the rate of feed.

(3) Compute the sodium hydroxide charge.

(4) Compute the water required to make a 30 percent solution with the sodium hydroxide charge specified.

17. Operating personnel.—*a.* The size of the operating force will depend on the size of the plant and on the speed required. The average plant will require—

- (1) One officer or noncommissioned officer in charge.
- (2) One engineer, noncommissioned officer.
- (3) Four privates, during operation.

b. The duties of the officer in charge will be—

(1) To arrange for the supply of all material necessary for the care and operation of the plant.

(2) To determine the amount of materials and to make sure that the proper amounts are used for the generation of the required amount of gas.

(3) To execute general supervision over the care, repair, and operation of the plant and to give the necessary directions to all members of the crew in order to insure the efficient use and conservation of materials.

c. The engineer should be directly responsible for all repairs on the plant, for the operation of the power plant, pumps, water supply, feed mechanism, and agitators.

d. The work of the privates will be about equally divided if two are assigned to the handling of the caustic soda and two to handling the ferrosilicon.

18. Care of plant.—*a. Inspection.*—The whole plant should be inspected periodically to locate any parts that should be replaced. If it is necessary to use dirty water, the pumps and washer should be frequently inspected to determine that they are not being filled with an accumulation of dirt.

b. Lubrication.—The engineer should be held responsible for the proper lubrication of gears and bearings of the whole plant.

c. Testing for leaks.—Even small leaks in the generator and piping may cause a considerable loss in gas and such leaks are a source of fire. The safest, quickest, and easiest method of locating leaks is by means of a fairly strong solution of soapsuds which can be easily applied over any suspected seam by means of a brush. (See par. 23.)

19. Precautions.—The following general precautions are to be observed in the operation of the generator:

a. No flames or other possible sources of ignition, such as unprotected electrical switches, are to be permitted in the generator house or in the immediate neighborhood of the generator.

b. The generator and all connections between the generator and the nurse balloon or gas storage must be made gastight and kept in perfect condition.

c. No white lead, red lead, or materials containing linseed oil should be used in the generator, because linseed oil dissolves in a sodium hydroxide solution with the formation of a soap, while lead oxide (red lead) and other compounds react with silicon under certain conditions with the production of heat sufficient to ignite a gas mixture.

d. Care should be taken never to introduce an excessive amount of ferrosilicon into the generator, especially when the generator is cold. The greatest danger lies in starting the ferrosilicon feed when the temperature is low and allowing it to run until either the temperature or the rate of gas production is brought up to the desired working condition. Such a procedure is similar to heaping fuel on a smoldering fire without regard to the result when the fire begins to burn vigorously. In either case the temperature and rate of reaction are certain to pass beyond the operator's control. The amount of ferrosilicon shown by experience to be best should be added at the start, and the reaction allowed to proceed without further addition of material until the working temperature is reached. Ferrosilicon may then be fed in at any desired rate without danger of accumulating a large excess; and the only conditions necessary to insure a regular evolution of gas are a regular ferrosilicon feed and a constant temperature, easily controlled by regulating the water spray.

e. The air must be swept out of the generator before the hydrogen is run into the balloon. The initial charge of ferrosilicon should be sufficient to accomplish this purpose. There is some danger of sparks being produced by moving metal parts, especially in the presence of a hard granular substance like ferrosilicon, and a spark produced before air is expelled sufficiently will blow up the generator. Consequently, neither the feeding nor the stirring mechanism should be started, and the gas produced should be run to waste until the working temperature is reached.

f. Men working around the plant, especially those handling the sodium hydroxide, should be protected by rubber gloves, goggles, and, preferably, rubber clothing, and face masks. Sodium hydroxide in the eyes may cause blindness. Keep a bottle of 2 percent acetic acid (vinegar) and plenty of absorbent cotton always convenient in a tightly inclosed container. In case of bad caustic burns, especially of the eyes, wash freely with acid. It would be well to have a bottle containing a saturated solution of boric acid with which to wash

the eyes thoroughly after using acetic acid. For washing the hands and face when the alkali has come in contact with the skin, weak vinegar may be used. Vinegar, which is merely dilute impure acetic acid, may also be used for washing the eyes, provided no pure acetic acid is at hand; but since the strength of vinegar is usually unknown and subject to change, and other substances may be present which will injure the eyes, acetic acid should always be used if obtainable.

SECTION III

TESTS

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20. Nature and frequency.—*a. General.*—Balloon gas must be tested to determine its lifting power and its purity. The lifting power is determined directly by the determination of the specific gravity. Contamination by other gases is determined by analysis for oxygen, carbon dioxide, etc. The determination of oxygen is especially important, since the presence of oxygen in amounts beyond certain limits will make the handling and use of the gas particularly hazardous. The determination of specific gravity not only enables the lifting power to be calculated therefrom, but is also an indication of the amount of other gases present, since all other gases are heavier than hydrogen. Therefore if the specific gravity is within allowable limits the determination of the oxygen content would be unnecessary to determine whether or not the gas was safe for handling.

b. Frequency.—The frequency with which hydrogen should be tested will depend on the source of the hydrogen and the immediate use which is to be made of it. Tests of purity should be made when there is any reason to suspect the presence of serious contamination.

21. Analysis.—*a. Absorption method, using alkaline pyrogallol.*—(1) *General.*—The gas to be analyzed is passed through and intimately mixed with chemicals that have the quality of absorbing certain gases. In the case of hydrogen the principal impurities to be checked are oxygen and carbon dioxide, other impurities not existing in sufficiently large quantities to warrant a thorough analysis. The percentage of oxygen mixed with hydrogen can be determined by means of apparatus shown in figure 1. Briefly, the method is to measure out a definite volume of the hydrogen in a burette *A* and then

pass it into the pipet *B*, which is filled with alkaline pyrogallol. When the oxygen is completely absorbed the gas is drawn back into the burette and the decrease in its volume is equal to the volume of oxygen originally present.

(2) *Setting up apparatus.*—The stopcocks should be well greased with a *very thin film* of vaseline. This is to make them gastight and

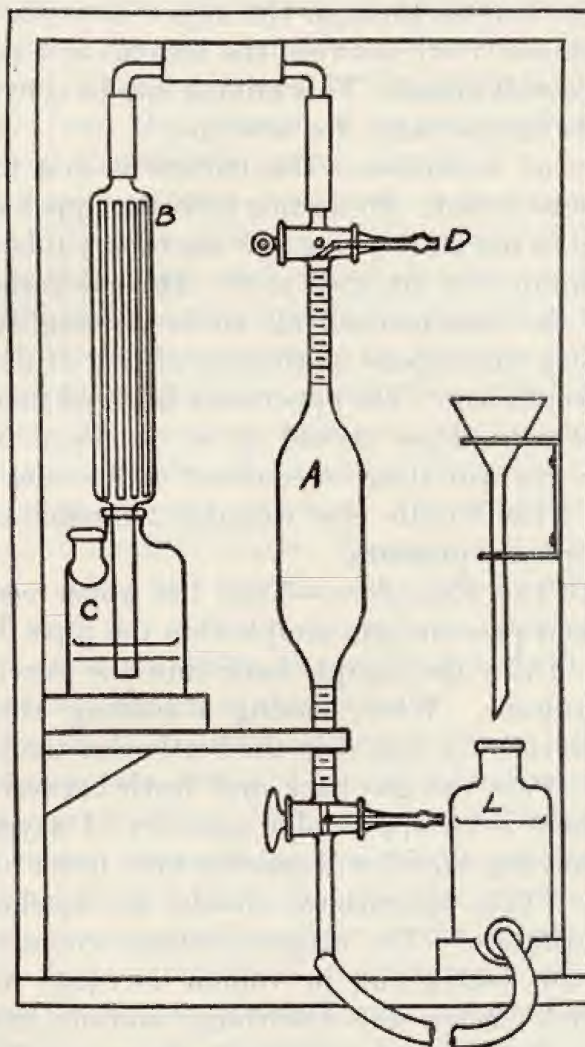


FIGURE 1.—Modified Orsat testing apparatus.

keep them from sticking. The leveling bottle *L* should be filled with clean water. Make up a solution of 6 grams of pyrogallol in 18 cubic centimeters of distilled water. In another vessel make up a solution of 140 grams of potassium hydroxide in 95 cubic centimeters of distilled water. By means of the funnel, introduce into the bottle *C* the solution of potassium hydroxide. Next pour in 30 cubic centimeters of light oil. This is to protect the reagent from the oxygen of

the atmosphere. Fill the burette with water by raising the leveling bottle with the upper cock open to the air. Then connect the burette with the pipet and by lowering the leveling bottle draw the potassium hydroxide up until it fills the capillary tube. This expels all air from the pipet. The pyrogallol is now introduced into the bottle *C* and allowed to mix intimately, or some other gas nearly *free from oxygen* is drawn into the burette through the upper stopcock. This gas is then passed back and forth between the burette and pipet until the two solutions are well mixed. This mixing can be conveniently done with the first gas sample taken for analysis.

(3) *Operation of apparatus.*—The burette is first filled with the sample of gas to be tested. To do this both the upper and the lower cocks are opened to the atmosphere and the rubber tube leading from the hydrogen container is attached at *D*. The gas is then allowed to stream through the burette until all air is thoroughly flushed out. The time necessary will depend on the rate of flow of the gas; usually 1 or 2 minutes is sufficient. The upper cock is closed first and then the lower cock is closed. They should never be closed in the reverse order, since the gas will then be confined under more than atmospheric pressure. The burette now contains 100 cubic centimeters of gas under atmospheric pressure.

(4) *Analysis.*—(a) *Procedure.*—Turn the upper cock to connect with the pipet and pass the gas sample into the pipet by raising the leveling bottle. Draw the sample back into the burette and again determine the volume. When making a reading always hold the leveling bottle so that the liquid in the bottle and the burette are on the same level. Pass the gas back and forth between burette and pipet. When there is an appreciable quantity of oxygen present in the gas, the absorbing liquid will quickly turn black or dark brown at the surface. This appearance should be watched for, as it is a reliable indication. The original sample contained 100 cubic centimeters so the contraction in volume is equal to the percent oxygen contained. Since the absorbing solution contains potassium hydroxide, any carbon dioxide in the gas will be absorbed as well as oxygen. The gas from a silicon generator will, however, be nearly free from carbon dioxide. The atmosphere usually contains less than 0.1 percent carbon dioxide, so that contamination by air would introduce a negligible quantity of carbon dioxide. If any of the pyrogallate solution is allowed to get into the burette, it should be washed out and the leveling bottle refilled with clean water before undertaking another analysis. This is to prevent any absorption of gas while the sample is in the burette.

(b) *Determination of carbon dioxide in hydrogen.*—The quantitative determination of carbon dioxide in hydrogen may be carried out by substituting for the solution of potassium pyrogallate a solution of sodium or potassium hydroxide (1 part of hydroxide to 2 parts of water). The manipulation is exactly the same as in the analysis for oxygen. The absorption of carbon dioxide will, however, take place more quickly than the absorption of oxygen by potassium pyrogallate. If the hydrogen contains carbon dioxide, this must be removed before testing for oxygen or the percentage of carbon dioxide subtracted from the amount of oxygen indicated because the oxygen absorbent also absorbs carbon dioxide.

(c) *Determination of carbon monoxide in hydrogen.*—For estimate of quantity of carbon monoxide in gas by means of an Orsat absorption apparatus, the oxygen and carbon dioxide are first extracted as described above and the gas containing carbon monoxide is passed into a solution of cuprous chloride in hydrochloric acid. This is prepared by pouring 250 cubic centimeters of concentrated hydrochloric acid over 35 grams of commercial cuprous chloride, placing some copper gauze in the solution, and keeping it protected from the air until it has turned colorless. The solution is then poured into 1.5 liters of distilled water, whereby white cuprous chloride is precipitated. After 24 hours the clear liquid above the precipitate is poured off and the cuprous chloride is dissolved in 250 cubic centimeters of ammonia water of specific gravity 0.91. The carbon monoxide present in the gas is absorbed.

b. *Absorption method using ammonia-copper solution.*—(1) *Apparatus.*—The apparatus required consists of a Hempel or other form of glass burette graduated at least as fine as 0.2 cubic centimeter and connected by rubber tubing or other means to an absorption pipet or aspirator bottle (preferably of 200 cubic centimeters capacity). The reagents required are metallic copper in the form of wire or gauze and a freshly made mixture of equal volumes of ammonia water (specific gravity 0.93) and a saturated aqueous solution of commercial ammonium sesquicarbonate. The solutions of ammonia and sesquicarbonate will be kept separately and a fresh supply of the mixture prepared daily. The test mixture is capable of absorbing about twenty-four times its volume of oxygen. It is advisable to clean the metallic copper before using by treatment for a moment with nitric acid and immediately washing free from acid with distilled water. The copper is used in a pipet or bottle in the usual manner employed for absorbents in gas analyses.

(2) *Method*.—Approximately 100 cubic centimeters of the sample will be taken for test and measured accurately over water saturated with oxygen or over mercury. The measured sample will then be transferred to the pipet or aspirator bottle containing the absorbents and allowed to remain 5 minutes, and then be transferred back to the burette and the volume read. This process is to be repeated until two consecutive readings agree within 0.1 cubic centimeter.

22. General determination of specific gravity.—*a.* The specific gravity of a gas is defined as the ratio of the weight of a given volume of gas to the weight of an equal volume of air, measured at the same temperature and pressure. In other words, it is the relative weight of the gas as compared with air. The specific gravity of a gas may be determined by several different methods. Apparatus operating by the effusion method is supplied for determining the specific gravity of hydrogen.

b. Principle of effusion method for specific gravity.—The effusion method for the determination of the specific gravity of a gas is based upon the fact that the times required for the escape of equal volumes of two gases under the same pressure through the same small orifice are approximately proportional to the square root of the densities of the gases. This relation is only an approximation, however, and the accuracy obtainable depends on the size and shape of the orifice and the operating conditions.

c. The Army effusion apparatus.—(1) The apparatus, figure 2, consists of a gas chamber, *C*, connected by a rubber tube at the bottom to a movable reservoir, *L*, which is held in a support as shown. The gas chamber is connected at the top to a 3-way cock, which allows the gas chamber to be connected with either the gas inlet, *I*, on the left or to tube, *O*, containing the orifice on the right. In brief, the method of operation is to measure the time required for a given volume of air to flow through the orifice under the pressure of the head of water in the reservoir and then to measure the time required for the same volume of the hydrogen to flow through the orifice. The orifice is made in a thin plate of platinum-iridium (thickness=0.04 mm.) and is 0.25 to 0.30 millimeter in diameter.

(2) *Operation.*—(*a*) The apparatus is set on a firm, level base. Distilled water is then introduced through the leveling bulb while this bulb is in position on its support and while the 3-way cock is set to connect the gas chamber with the surrounding atmosphere. Enough water should be introduced to fill the apparatus to the mark on the glass a few centimeters below the stopcock. The water jacket should be filled with water and the whole apparatus

allowed to come to room temperature before starting a test. Care should be taken that the apparatus is kept at a constant temperature during any test, and no water should be lost from, or added to, the apparatus during a test. For each test the temperature of the water in the jacket surrounding the gas chamber should be observed in order to permit correction of the observed specific gravity.

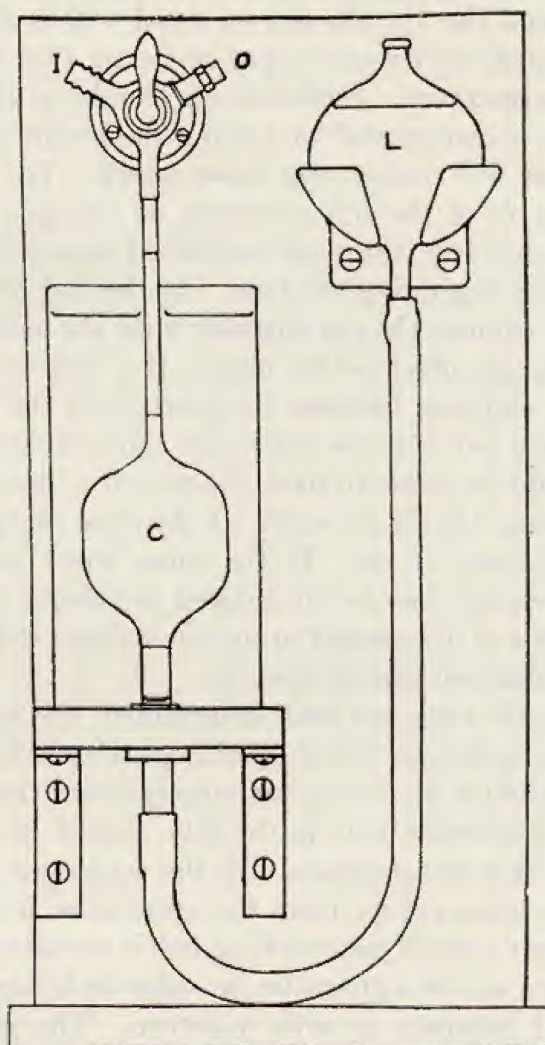


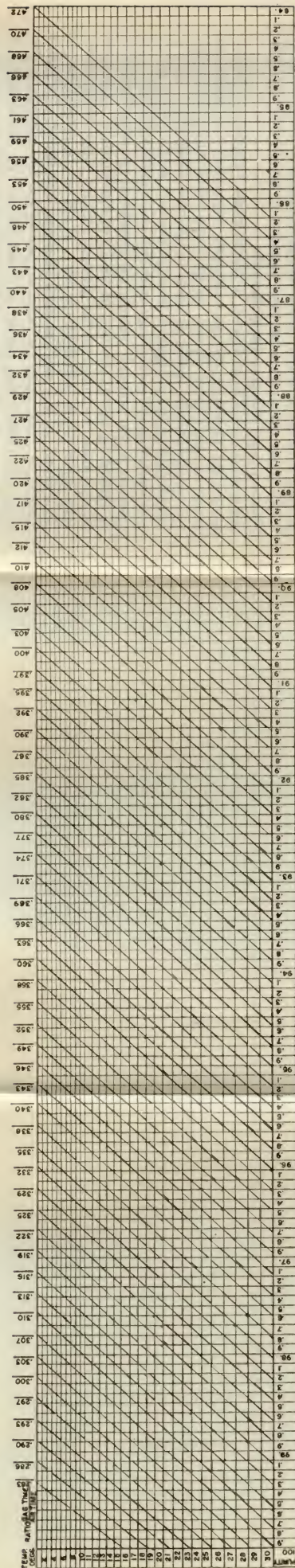
FIGURE 2.—Army apparatus for testing specific gravity of gases.

(b) The orifice tube should be screwed in position on the 3-way cock and tightened with a small wrench. It is very important that the orifice tube fit gastight, since if there is a small leak at the base the results will be erroneous. When not in use, the orifice tube should be protected from dust and moisture by attaching its cover. It should never be left on the apparatus unless the cock is turned to shut off connection with the gas chamber. This is to prevent the condensation

of water vapor in the orifice. The orifice tube should be kept on the screw plug in the base of the apparatus which is intended to serve as a holder.

(c) To make the test, the gas chamber is filled with a sample of air drawn in through the side connection of the 3-way cock by lowering the leveling bulb. The cock is then closed, the leveling bulb placed on its support, and the air allowed to stand within the gas chamber to become saturated with water vapor to insure that it is at the temperature of the apparatus. Sufficient air should be drawn in so that when the sample is compressed by raising the leveling bulb the water level will remain well below the lower mark. To insure that the water will drain from the inner surface of the gas chamber to the same extent in each test, the same period of time should be allowed after filling before beginning the test. At the end of this period the cock is turned to connect the gas chamber with the orifice and the time of effusion of the air observed by means of a stop watch. The time observed is that elapsing between the passage of the water meniscus from the mark just below to the mark just above the gas chamber. In timing care should be taken to have the eye on a level with the mark. *Ten determinations should be made of the time required for the effusion of this volume of air.* If the times check within two-fifths second, the agreement may be considered satisfactory. It should be noted that an error of 0.5 percent in timing makes a difference of about 1 percent in the apparent specific gravity.

(d) After the air time has been determined, the apparatus should be filled with the hydrogen whose specific gravity is to be determined. This hydrogen should be at approximately room temperature when taken into the apparatus and preferably should be saturated with water vapor at this temperature. If the hydrogen is very dry or at very different temperature from the apparatus, it is convenient to draw it in through a small gas-washing bottle containing water at the same temperature as the apparatus in order to bring it to the right temperature and saturate it with moisture. The gas to be tested should be allowed to flow through the supply tube until all the air has been swept out, and while the gas is gently flowing the supply tube is attached to the inlet tube of the apparatus. The gas chamber is filled by lowering the leveling bottle, as was done with the air, and then allowing the hydrogen to flow out through the orifice. This rinsing of the gas chamber should be done three times to insure a sample uncontaminated by air. The time for effusion of the given volume of hydrogen is then determined in exactly the same manner as with air.



LEGEND — DIVIDE AIR TIME BY GAS TIME. LOCATE ON RATIO LINE. FOLLOW DIAGONAL TO HORIZONTAL TEMPERATURE LINE THEN READ PURITY ON BOTTOM OF VERTICAL LINE.
GAS PLANT SCOTT FIELD, ILL.

PURITY CHART HYDROGEN
CONVERSION TABLE FOR SPECIFIC GRAVITY SATURATED GAS TO DRY GAS.

(e) If the time of effusion with either hydrogen or air is irregular from test to test, this may be the result of moisture condensed in the orifice. This moisture can be removed by blowing dry air through the orifice. Care must be taken at all times to keep the orifice free from dust or other material that will change its size or shape. Especial care should be taken to prevent water from getting into the cock, since it may be blown into the orifice and cause serious trouble.

d. Calculation of specific gravity.—The specific gravity of a dry gas referred to dry air is, for all practical purposes, the same for any temperature. But the specific gravity of dry hydrogen compared with dry air is always different from the specific gravity of saturated hydrogen at different temperatures and pressures. The specific gravity of the hydrogen under the conditions of test is the ratio of the square of the time for hydrogen effusion to the square of the time for air effusion; that is,

$$S_s = \frac{(T_h)^2}{(T_a)^2}$$

The following shows the relation between the specific gravities of saturated hydrogen compared with saturated air and the specific gravity of dry gas referred to dry air:

$$S_s = \frac{(S+k)}{(1+k)}$$

$$S = S_s (1+k) - k$$

S = specific gravity of dry gas referred to dry air.

S_s = specific gravity of saturated hydrogen referred to saturated air.

The values of k for gas at 760 mm. pressure and at various temperatures are as follows:

Temperature	k
0° C.....	0.004
5° C.....	.005
10° C.....	.008
15° C.....	.011
20° C.....	.015
25° C.....	.020

The following is an example of the use of these formulae:

The specific gravity, S , of pure, dry hydrogen is 0.0695. The specific gravity of saturated hydrogen, S_s , at 20° C. is

$$S_s = \frac{0.0695 + 0.015}{1 + 0.015} = 0.0833$$

This is the value which the effusion apparatus would give at 20° C. with pure hydrogen. The following table may be used to obtain accurately the purity of a gas knowing the effusion times and temperature.

23. Short hydrogen-leak detector.—The short hydrogen-leak detector consists primarily of a closed chamber connected to a sensitive pressure gage. One side of this chamber is composed of porous material. The instrument in form is circular and flat, having a grating on its underside which protects the porous diaphragm from shock. On the back of the instrument is situated a small gage with a pointer registering on an ungraduated dial. A small pet cock is screwed into the chamber connected with the gage by means of which pressure may be released. This instrument is provided with a handle and can be attached to a bamboo pole in order to explore such points as may be out of reach of the inspector. The action of the instrument is based on the different rates of diffusion of hydrogen and air. Thus, when it is exposed to an atmosphere containing hydrogen, the hydrogen diffuses through the porous wall of the closed chamber at a rapid rate and a pressure is built up within, which is indicated by the pressure gage. The instrument is run over the fabric of a balloon and leaks will be detected by the movement of a pointer in the gage, showing an increase of pressure in the chamber. This pressure should then be released by opening the pet cock; the instrument is then ready for further inspection. If some hydrogen remains in the chamber covered by the porous diaphragm and if the pet cock is kept closed and the instrument brought into an atmosphere containing no hydrogen, the hydrogen will diffuse outward, again reducing the pressure in the chamber and giving a negative reading on the gage. Therefore, the pet cock should be left open for a few moments to allow the hydrogen to be replaced by the air. It should be noted that gases lighter than air will diffuse through the instrument and produce a positive reading, but when the instrument is exposed to an atmosphere containing gases heavier than air, such as CO_2 , a negative reading will be indicated, as diffusion will be in the opposite direction.

24. Testing qualitatively for impurities.—*a.* Phosphine, PH_3 , and arsine, AsH_3 , are sometimes found in hydrogen generated by silicon method. Treat six filter papers with silver nitrate, AgNO_3 , and ammonia, aqueous, NH_3 . These papers are held in a current of the gas; a brownish gray color indicates phosphine and a deep gray indicates arsine.

b. Hydrogen sulfide, H_2S , is sometimes found in hydrogen generated by the silicon method. Impinge gas on filter papers wet with acetate of lead (sugar of lead). A brown discoloration takes place if hydrogen sulfide is present.

c. To test for carbon dioxide, pass gas through an aspirator bottle in which is contained 1 part by weight of potassium hydroxide,

KOH, dissolved in 6 parts by weight of distilled water. In the presence of carbon dioxide the solution will become milky.

d. To test for carbon monoxide, impinge the gas on filter paper moistened with palladium protochloride solution. The blackening of the paper indicates the presence of carbon monoxide.

e. To test for chlorine, pass the gas through 20 cubic centimeters of a freshly prepared colorless solution of potassium iodide. In the presence of free chlorine (or bromine) the iodide solution is changed to a brown color.

Conversion table of Fahrenheit to centigrade

F.	C.	F.	C.	F.	C.	F.	C.
-40	-40	56	13.3	128	53.3	200	93.3
-30	-34.4	58	14.4	130	54.4	202	94.4
-20	-28.9	60	15.6	132	55.6	204	95.6
-10	-23.3	62	16.7	134	56.7	206	96.7
-8	-22.2	64	17.8	136	57.8	208	97.8
-6	-21.1	66	18.9	138	58.9	210	98.9
-4	-20	68	20	140	60	212	100
-2	-18.9	70	21.1	142	61.1	214	101.1
0	-17.8	72	22.2	144	62.2	216	102.2
2	-16.7	74	23.3	146	63.3	218	103.3
4	-15.6	76	24.4	148	64.4	220	104.4
6	-14.4	78	25.6	150	65.6	222	105.6
8	-13.3	80	26.7	152	66.7	224	106.7
10	-12.2	82	27.8	154	67.8	226	107.8
12	-11.1	84	28.9	156	68.9	228	108.9
14	-10	86	30	158	70	230	110
16	-8.9	88	31.1	160	71.1	232	111.1
18	-7.8	90	32.2	162	72.2	234	112.2
20	-6.7	92	33.3	164	73.3	236	113.3
22	-5.6	94	34.4	166	74.4	238	114.4
24	-4.4	96	35.6	168	75.6	240	115.6
26	-3.3	98	36.7	170	76.7	242	116.7
28	-2.2	100	37.8	172	77.8	244	117.8
30	-1.1	102	38.9	174	78.9	246	118.9
32	0	104	40	176	80	248	120
34	1.1	106	41.1	178	81.1	250	121.1
36	2.2	108	42.2	180	82.2	260	126.7
38	3.3	110	43.3	182	83.3	270	132.2
40	4.4	112	44.4	184	84.4	280	137.8
42	5.6	114	45.6	186	85.6	290	143.3
44	6.7	116	46.7	188	86.7	300	148.9
46	7.8	118	47.8	190	87.8	400	204.4

Conversion table of Fahrenheit to centigrade—Continued

F.	C.	F.	C.	F.	C.	F.	C.
48	8.9	120	48.9	192	88.9	500	260
50	10	122	50	194	90	750	398.9
52	11.1	124	51.1	196	91.1	1,000	537.8
54	12.2	126	52.2	198	92.2	2,000	1,093.3

Absolute temperature: -459.6° F. = 273° C.

Freezing point: 32° F. = 0° C.

Boiling point: 212° F. = 100° C.

[A. G. 062.11 (6-25-40).]

BY ORDER OF THE SECRETARY OF WAR:

G. C. MARSHALL,
Chief of Staff.

OFFICIAL:

E. S. ADAMS,
Major General,
The Adjutant General.

